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(54) Title: INTERNAL MOULD RELEASE COMPOSITION (57) Abstract <p>An internal mould release composition which comprises: (a) at least one carboxylic acid metal salt wherein said carboxylic acid contains from 2 to 30 carbon atoms and wherein said metal is selected from Group II of the Periodic Table of the Elements; (b) at least one compatibilizer which compatibilizes said carboxylic acid metal salt in a polyol; and (c) jojoba oil, is disclosed. This internal mould release composition exhibits excellent mould release properties and does not degrade a polyurethane catalyst in a fully formulated RIM system.</p>		

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INTERNAL MOULD RELEASE COMPOSITION

The present invention relates to an internal mould release composition particularly useful in the reaction injection moulding (RIM) of polyurethane and polyurea products.

Reaction injection moulding is a versatile process by which elastomeric and thermoset products can be fabricated. The moulded products are prepared by injecting a mixture of polyurethane foam forming components into a mould which is usually closed and heated. The foam-forming mixture is allowed to react and a foam which is formed within the mould solidifies whilst being compressed within the mould, so that a foamed product corresponding to the shape of the inside of the mould is formed. The mould is then opened and the product is removed from the mould. The problem exists, however, in providing adequate mould release in the shortest possible time to take fullest advantage of the unique capabilities of the RIM process.

Release of molded products from moulds in which they have been formed has been achieved by coating the surface of the mould cavity with an agent which facilitates release of the moulded product from the walls of the mold cavity. Procedures such as this are described in U.S. Patents 3,694,530; 3,640,769; 3,624,190; 3,607,397 and 3,413,390. This method has certain disadvantages. The agent, after moulding, adheres to the surface of the moulded article thereby removing such from the surface of the mould. As the mold release agent is removed from the mould surface, it must be replaced so as to provide continued release of the moulded articles from the mould. The necessity for reapplying the release agent after each molding or a limited number of moldings interrupts the molding operation, slows down output and results in higher costs due to low productivity. Also, the presence of the release agent adhering to the surface of the moulded product can impede subsequent operations on the product, such as painting or adhering operations.

The use of internal mould release agents in moulding polyurethane and polyurea products has been disclosed in numerous patents.

U.S. Patents 4,201, 847 and 4,254,228 describe an internal mould release agent which is the reaction product of an organic polyisocyanate and an active hydrogen containing high fatty acid ester.

U.S. Patents 4,519,965; 4,581,386; 4,585,803 and 4,764,537; and British Patent 2,101,140 describe the use of zinc carboxylates containing from 8 to 24 carbon atoms per carboxylate group as internal mould release agents.

European Patent 0 364 846 A2 describes an internal mould release composition comprising the reaction product of an organic polyisocyanate with active hydrogen containing high fatty acid ester and the mixture comprising zinc carboxylates containing from 8 to 24 carbon atoms per carboxylat group and a compatibilizer for same such as an amine-based

polyether, for example, Jeffamine D-400, as an internal mould release agent. This internal mould release composition is said to allow release of the product from a bare metal mould.

U.S. Patent 4,130,698 describes a mould release composition which consists essentially of 99.9 percent by weight of an aromatic polyisocyanate containing at least two isocyanate groups and 0.1 percent to 20 percent by weight of a fatty acid ester, for example, glycerol trioleate, olive oil, peanut oil, coconut oil, rape seed oil, and sunflower seed oil.

U.S. Patent 3,726,952 describes an internal mould release composition which is a salt of an aliphatic carboxylic acid and a primary amine or amine-containing amide or ester groups containing a total of at least 25 aliphatic carbon atoms distributed between the amine and the carboxylic acid. While showing release characteristics per se, their use has demonstrated in a screening program wherein hand mixed formulations are cast into an open mold other serious problems, namely: (1) degradation of the tin catalyst employed in the formulation, (2) excessively long gel and cure time, and (3) poor physical properties. These problems are believed to be caused by the presence of free carboxylic acid. It is released from the salt by the reaction of the amine with the isocyanate, and it is believed that the presence of these free carboxylic acids, or any acid, interferes with the cure rate of the hydroxyl/isocyanate reaction to form a urethane structure as disclosed in J. Polymer Science, Polymer Chemistry Edition, Vol. 19, pp. 381-388 (1981) John Wiley & Son, Inc.

The reactivity or catalyst kill problem can be overcome to a certain degree by using tertiary amines in place of primary or secondary amines. Both U.S. Patents 3,726,952 and 4,098,731 describe this technique. Since isocyanates cannot react with tertiary amines the salt cannot be split; it thus remains neutral (the carboxylic acid is not free), hence, catalyst kill does not seem evident. The use of tertiary amines, however, often shows bleed out or exudation problems which in turn result in poor paint adhesion. Further, retention of physical properties is seldom possible because of either excess reactivity when using very catalytically active amines, or because of plasticizer effects brought about by excessively long tertiary amine molecules.

U.S. Patent 4,111,861 discloses that polar metal compounds can be employed to overcome catalyst kill problems brought on by the presence of fatty carboxylic acids. It discloses that metal ions must be present in an amount sufficient to neutralize the acid. Reference is made to the use of the Bi, Pb, Na, Li, and K ion, with sodium carbonate, sodium oleate, and potassium laurate being exemplified. They also show sodium oleate alone to be an effective release agent. When evaluated in RIM polyol systems as a single additive, it failed to show adequate release characteristics in a screening program wherein hand mixed formulations were cast into an open mold.

Zinc stearate has long been known to be an effective release agent for most thermoplastics. It is also used in polyester sheet molding compounds. When evaluated in RIM polyol systems containing only hydroxyl groups as the active hydrogen-containing source, zinc

stearate as a single additive failed to show adequate release characteristics in a screening program wherein hand mixed formulations were cast into an open mold. Zinc stearate dissolved in aliphatic amines, such as polyether amines and ethylenediamine-initiated polyols, has been used as an effective internal mould release agent. Also, zinc soaps can be compatibilized or dissolved in polyol blends with amines, enamines, ketimines or salts of amidines or guanidines and such composition perform as internal mould release agents.

U.S. Patent 4,876,019 describes an internal mould release composition which comprises (a) at least 1 percent by weight of said composition of at least one metal salt of an organic material containing at least one carboxylic acid group or mixtures of such materials; (b) a material containing at least one primary amine group and/or at least one secondary amine group per molecule or a mixture of such materials, and optionally; and (c) at least one organic material containing at least one carboxylic acid group, phosphorus- or boron-containing acid group or mixture of such materials wherein the organic material contains a backbone of siloxane chains or contains at least one terminal or pendant saturated or unsaturated aliphatic hydrocarbon chain containing at least 7 carbon atoms, for example, zinc stearyl sarcosinate and zinc oleoyl sarcosinate.

U.S. Patents 5,008,033 and 5,011,674 describe an active hydrogen-containing composition comprising (a) a material having an average of at least 2 active hydrogen-containing groups per molecule and a weight from 500 to 5000 per active hydrogen-containing group, said composition having dissolved therein (b) from 0.5 to 10 parts by weight per 100 parts by weight of component (a), of a metal salt of an organic material containing at least one carboxylic acid group and a saturated or unsaturated aliphatic hydrocarbon chain having at least 7 carbon atoms or a siloxane chain; and a process comprising reacting a polyisocyanate in a closed mould with the aforementioned active hydrogen-containing composition.

U.S. Patent 5,051,466 describes an internal mould release composition which comprises (a) at least one metal salt of an organic material derived from a material containing at least one carboxylic acid group, phosphorus- or boron-containing acid group or mixture of such materials and wherein the organic material contains a backbone of siloxane chains or contains at least one terminal or pendant saturated or unsaturated aliphatic hydrocarbon chain containing at least 7 carbon atoms; (b) a material containing at least one primary amine group and/or at least one secondary amine group per molecule or a mixture of such materials, and optionally; (c) at least one organic material containing at least one carboxylic acid group, phosphorus- or boron-containing acid group or mixture of such materials wherein the organic material contains a backbone of siloxane chains or contains at least one terminal or pendant saturated or unsaturated aliphatic hydrocarbon chain containing at least 7 carbon atoms.

U.S. Patent 5,045,591 describes a process for preparing polymeric products which process comprises mixing and injecting into a suitable mould an "A-side" component comprising a polyisocyanate and/or polyisocyanate and a "B-side" component comprising at

least one material containing at least one primary and/or secondary amine group per molecule or a mixture of such materials, and a metal salt of a carboxy functional siloxane consisting essentially of from 0.5 to 20 mol percent of $RaR'bSiO_{4-a-b/2}$ units and from 80 to 99.5 mole percent of $R''cSiO_{4-c/2}$ units wherein R is carboxy functional radical, a has an average value from 1 to 3, R' is a hydrocarbon or substituted hydrocarbon radical, b has an average value from 0 to 2, the sum of a + b is from 1 to 3, R'' is a hydrocarbon or substitute hydrocarbon radical, and c has an average value from 0 to 3.

It has now surprisingly been discovered that a mixture of a metal salt of a carboxylic acid and jojoba oil performs not only as an effective internal mould release agent but also does not degrade the polyurethane catalyst in fully formulated RIM system.

In one aspect the present invention concerns an internal mould release composition comprising (a) at least one carboxylic acid metal salt wherein said carboxylic acid contain from 2 to 30, preferably from 2 to 21, carbon atoms and wherein said metal is selected from Group II of the Periodic Table of the Elements; (b) at least one compatibilizer which compatibilizes said carboxylic acid metal salt in a polyol; and (c) jojoba oil.

In another aspect the present invention concerns a polyol composition comprising (a) at least one polyol; (b) at least one carboxylic acid metal salt wherein said carboxylic acid contain from 2 to 30, preferably from 2 to 21, carbon atoms and wherein said metal is selected from Group II of the Periodic Table of the Elements, (c) at least one compatibilizer which compatibilizes said carboxylic acid metal salt in the polyol, and (d) jojoba oil.

In yet another aspect the present invention concerns a process for preparing polyurethane and/or polyurea products which process comprises mixing and injecting into a suitable mold a polyisocyanate and/or polyisothiocyanate component and a polyol component, allowing the components to react in the mould and then removing the resulting moulded product which process is characterized by incorporating the aforementioned internal mould release composition in the polyol component.

Any reference herein to the Periodic Table of the Elements refers to that published by Sargent-Welch Scientific Company as catalog number S-18806, 1968.

The internal mould release composition of the present invention is conveniently prepared by preblending (a) at least one carboxylic acid metal salt wherein said carboxylic acid contain from 2 to 30, preferably from 2 to 21, carbon atoms and wherein said metal is selected from Group II of the Periodic Table of the Elements with (b) at least one compatibilizer which compatibilizes said carboxylic acid metal salt in a polyol at an elevated temperature, usually at a temperature between 60°C and 100°C, and then adding to this blend (c) jojoba oil.

The internal mould release composition of the present invention can also be prepared by blending together, at an elevated temperature, usually at a temperature between 60°C and 100°C, (a) at least one carboxylic acid metal salt wherein said carboxylic acid contain from 2 to 30, preferably from 2 to 21, carbon atoms and wherein said metal is selected from

Group II of the Periodic Table of the Elements, (b) at least one compatibilizer which compatibilizes said carboxylic acid metal salt in a polyol, and (c) j joba oil.

Suitable carboxylic acid metal salts which can be employed as a component in the internal mold release composition of the present invention include those containing the metal ions from Group II metals. The carboxylic acid portions of these salts are suitably saturated or unsaturated having from 2 to 30, preferably from 2 to 21 carbon atoms. Particularly suitable carboxylic acids metal salts include, for example, zinc stearate, zinc oleate, zinc palmitate, zinc laurate, calcium stearate, calcium oleate, calcium palmitate, calcium laurate, magnesium stearate, magnesium oleate, magnesium laurate, magnesium palmitate and mixtures thereof. Zinc stearate is particularly preferred for use in the internal mold release composition of the present invention.

The carboxylic acid metal salt is conveniently used in an amount of from 1 percent to 50 percent, preferably from 5 percent to 33 percent, most preferably from 10 percent to 25 percent, based on the weight of the internal mould release composition.

The jojoba oil is conveniently used in an amount of from 1 percent to 40 percent, preferably from 10 percent to 30 percent, most preferably from 10 percent to 20 percent, based on the weight of the internal mould release composition.

Any known polyol or a mixture of one or more polyols can be employed in the polyol composition of the present invention. The polyol is often prepared by the catalytic condensation of an alkylene oxide or mixture of alkylene oxides either simultaneously or sequentially with an organic compound having at least two active hydrogen atoms, such as evidenced by U.S. Patents 1,922,459; 3,190,927; and 3,346,557.

Suitable polyols which can be employed in the present invention include polyether and polyester polyols, and alkylene oxide adducts of polyhydric polythioesters, polyacetals, aliphatic polyols and thiols, ammonia, and amines including aromatic, aliphatic, and heterocyclic amines, as well as the mixtures thereof. Alkylene oxide adducts of compounds which contain 2 or more different groups within the above-defined classes may also be used, for example, amino alcohols which contain an amino group and a hydroxyl group. Also, alkylene oxide adducts of compounds which contain one SH group and one OH group as well as those which contain an amino group and an SH group may be used. Generally, the polyols will have an average hydroxyl functionality of from 2 to 8, preferably from 2 to 4 and an equivalent weight of from 500 to 10,000, preferably from 1000 to 3000.

Suitable polyester polyols which may be employed herein include, for example, those prepared by reacting a polycarboxylic acid or anhydride thereof with a polyhydric alcohol. The polycarboxylic acids may be aliphatic, cycloaliphatic, aromatic and/or heterocyclic and may be substituted (for example, with halogen atom) and/or unsaturated. Examples of carboxylic acids of this kind include succinic acid; adipic acid; suberic acid; azelaic acid; sebacic acid; phthalic acid; isophthalic acid; trimellitic acid; phthalic acid anhydride;

tetrahydrophthalic acid anhydride; hexahydrophthalic acid anhydride; tetrachlorophthalic acid anhydride; endomethylene tetrahydrophthalic acid anhydride; glutaric acid anhydride; maleic acid; maleic acid anhydride; and fumaric acid. Mixtures of such acids or anhydrides may also be employed. Examples of suitable polyhydric alcohols include ethylene glycol, 1,2-
 5 propylene glycol; 1,3-propylene glycol; 1,4-, 1,2- and 2,3-butylene glycol; 1,6-hexane diol; 1,8-octane diol; neopentyl glycol; cyclohexane dimethanol (1,4-bis-hydroxymethyl cyclohexane) 2-methyl-1,3-propane diol; glycerol; trimethylol propane; 1,2,6-hexane triol; 1,2,4-butane triol; trimethylol ethane; pentaerythritol; quinitol; mannitol; sorbitol; methyl glycoside; diethylene glycol; triethylene glycol; tetraethylene glycol; polyethylene glycol; dipropylene glycol;
 10 polypropylene glycols; dibutylene glycol and polybutylene glycols. The polyesters may contain some terminal carboxyl groups. It is also possible to use polyesters of lactones such as caprolactone, or hydroxy carboxylic acids such as hydroxy caproic acid.

Suitable polyether polyols are prepared by reacting at least one alkylene oxide, halogen substituted or aromatic substituted alkylene oxides or mixtures thereof with an active
 15 hydrogen-containing initiator compound. Suitable initiator compounds include water, ethylene glycol, propylene glycol, butanediol, hexanediol, glycerine, trimethylol propane, pentaerythritol, hexanetriol, sorbitol, sucrose, hydroquinone, resorcinol, catechol, bisphenols, novolac resins, phosphoric acid, and mixtures thereof. Suitable initiators also include ammonia, ethylenediamine, diaminopropanes, diaminobutanes, diaminopentanes,
 20 diaminohexanes, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, ethanolamine, aminoethylethanolamine, aniline, 2,4-toluenediamine, 2,6-toluenediamine, diaminodiphenyl oxide (oxydianiline), 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, 1,3-phenylenediamine, 1,4-phenylenediamine, naphthylene-1,5-diamine, triphenylmethane-4,4',4"-triamine, 4,4'-di(methylamino)-
 25 diphenylmethane, 1-methyl-2-methylamino-4-aminobenzene, 1,3-diethyl-2,4-diaminobenzene, 2,4-diaminomesitylene, 1-methyl-3,5-diethyl-2,4-diaminobenzene, 1-methyl-3,5-diethyl-2,6-diaminobenzene, 1,3,5-triethyl-2,6-diaminobenzene, 3,5,3',5'-tetraethyl-4,4'-diamino-diphenylmethane and amine aldehyde condensation products such as the polyphenylpolymethylene polyamines produced from aniline and formaldehyde, and mixtures
 30 thereof.

Other suitable polyols which can be employed herein include polymer-modified polyols known as polymer (copolymer) polyols, PIPA polymer polyols and PHD polymer polyols.

Polymer (copolymer) polyols are produced by polymerizing or copolymerizing at least one ethylenically unsaturated monomer in the base polyol at elevated temperatures in
 35 the presence of a free-radical initiator. Preferred ethylenically unsaturated monomers include styrene and acrylonitrile. This type of polymer modified polyols is described U.S. Patent 3,304,273.

PIPA polymer polyols are prepared by polymerizing an olamine (that is, a compound containing at least one hydroxyl group and at least one amino group, whether primary, secondary or tertiary amino group) with an organic polyisocyanate in the presence of a polyol. This type of polymer modified polyols is described in British Patent 2,072,204.

5 PHD polymer polyols are prepared by the polyaddition reaction of a polyamine, or hydrazine with a mono or polyfunctional isocyanate in the presence of a polyol. This type of polymer modified polyols is described in British Patent 1,501,172.

Suitable polyhydric polythioethers which may be condensed with alkylene oxides include the condensation product of thiodiglycol or the reaction product of a dicarboxylic acid
10 such as disclosed above for the preparation of polyester polyols with any other suitable thioether glycol.

Polyhydroxyl-containing phosphorous compounds which may be used include those those compounds disclosed in U.S. Patent 3,639,542.

Suitable polyacetals which may be condensed with alkylene oxides include the
15 reaction product of formaldehyde or other suitable aldehyde with a dihydric alcohol or an alkylene oxide such as those disclosed above.

Suitable aliphatic thiols which may be condensed with alkylene oxides include alkanethiols containing one or two -SH groups such as 2-mercaptoethanol, 1,2-ethanedithiol, 1,2- and 1,3-propanedithiol, and 1,6-hexanedithiol; alkene thiols such as 2-butene-1,4-dithiol;
20 and alkyne thiols such as 3-hexyne-1,6-dithiol.

Examples of suitable amines which may be condensed with alkylene oxides include aromatic amines such as aniline, o- and p-chloroaniline, 1,5-diaminonaphtalene, and aliphatic amines such methylamine, triisopropanolamine, ethylene diamine, 1,3-diaminopropane, 1,3- and 1,4-diaminobutane, and ammonia.

25 The internal mould release composition of the present invention also contain a compatibilizer which assists or solubilizes the carboxylic acid metal salt in the polyol composition. Such compatibilizers are well known in the art. Suitable compatibilizers include nitrogen-containing, isocyanate-reactive, acyclic compounds such as aliphatic polyamines and nitrogen-containing isocyanate-reactive polymers, preferably polyethers. Preferred
30 compatibilizers include polyether polyamines and amine- or hydroxy-terminated, amine-initiated polyethers. Examples of these nitrogen-containing, isocyanate-reactive polymers include polyoxypropylene diamines (supplied as Jeffamine D-400 and Jeffamine D-2000 from Texaco), and polyoxypropylene triamines (supplied as Jeffamine T-403 and Jeffamine T-5000 from Texaco).

35 The organic polyisocyanates which are useful as the "A-side" component in the improved process of the present invention include those containing at least two isocyanate groups per molecule. Preferably, the polyisocyanate employed contains an average of from 2.0 to 3.0 isocyanate groups per molecule. Suitable polyisocyanates include aromatic

polyisocyanates, aliphatic, cycloaliphatic and heterocyclic polyisocyanates used alone or in admixture. The preferred polyisocyanates used in the practice of this invention are aromatic polyisocyanates and include the toluene diisocyanates, especially 2,4- and 2,6-toluene diisocyanate (TDI) as well as any desired mixture of these isomers; 2,4'- and 4,4'-

5 diphenylmethane diisocyanate (MDI) as well as any desired mixture of these isomers; oligomers of MDI (polymeric MDI), polymethylene polyphenyl polyisocyanates (commonly referred to as "crude MDI"); mixtures of TDI and polymeric MDI, and mixtures of these polyisocyanates. Prepolymers of the above polyisocyanate (for example, with polyether polyols, glycols or mixtures of these) can also be used in the present invention.

10 Mixtures of catalysts may also be employed in the process of the present invention. Such mixtures of catalysts include mixtures of two or more tertiary amines, mixtures of two or more organometallic compounds and mixtures of at least one tertiary amine with at least one organometallic compound.

Any catalyst known to promote the formation of urea and/or urethane linkages
15 of the polyurethane polymer may be used in the present invention. Suitable catalysts are those known to those skilled in the art of preparing polyurethane polymers and include tertiary amines and organometallic compounds. Examples of suitable tertiary amines include N-alkylmorpholines, such as N-ethylmorpholine, N,N-dialkylcyclo-hexylamines where the alkyl groups are methyl, ethyl, propyl and butyl, trialkylamines such as triethylamine,
20 tripropylamine, tributylamine and triamylamine, triethylenediamine, bis(2-dimethyl-aminoethyl)ether and N,N-dimethylaminoethyl-N',N'-dimethylaminopropyl ether. Examples of suitable organometallic compounds include carboxylic acids salts of tin, bismuth, or zinc such as stannous octoate, stannous acetate, stannous laurate and dialkyl tin salts such as dibutyl tin dilaurate and dibutyl tin maleate. The levels of catalyst used are conventional and typically
25 range from 0.01 to 3 parts by weight per 100 parts of total polyol present. Mixtures of catalysts may also be employed in the present invention.

If desired, the densities of the polyurethanes produced according to the present invention can be reduced by incorporating a blowing agent into the formulation. These blowing agents are used in amounts well known to skilled persons. Suitable blowing agents
30 are fully described in U.S. Patents 4,125,487 and 3,753,933. Suitable blowing agents include certain halogen- and non-halogen- substituted aliphatic or cycloaliphatic hydrocarbons having boiling points ranging from -40°C to +100°C including methylene chloride, volatile fluorocarbons and chlorofluorocarbons, for example, trichlorofluoromethane, dichlorodifluoromethane and 1-chloro-2-fluoroethane and low boiling hydrocarbons, for
35 example, n-propane, cyclopropane, butane, isobutane, pentane, hexane, cyclohexane and their mixtures.

Another suitable method for reducing the density is frothing by injecting an inert gas into the reaction components. Suitable such inert gases include, for example, nitrogen,

xygen, carbon dioxide, xenon, helium, mixtures thereof such as air and the like. These crosslinkers are used in amounts well known to skilled persons.

Known crosslinkers and/or chain extenders may be used in the present invention to modify polyurethane foam properties. Suitable crosslinkers include glycerine, diethanol amine and triethanol amine. Suitable chain extenders include ethylene glycol, diethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, 1,4-butane diol and diethyl toluene diamine. The crosslinkers and chain extenders are used in amounts well known to skilled persons.

If desired, foam stabilizers, surfactants or other cell control agents well known in the art can be employed, particularly when preparing foams or microcellular products of reduced density and/or to assist in paintability of the polyurethane. Suitable cell control agents and/or surfactants which can be employed herein include diverse silicone surfactants, preferably those which are block copolymers of a polysiloxane and a polyoxyalkylene as described in U.S. Patent 3,629,308. Exemplary of such surfactants are the products Tegostab B-4113 and B-8681 available from Th. Goldschmidt AG. The foam stabilizers, surfactants, cell stability or other cell control agents are used in amounts well known to skilled persons. Mixtures of one or more stabilizers and/or one or more surfactants may also be used.

The polyurethane products may additionally contain, if desired, coloring agents, fire retardant agents, fillers, and modifiers.

Suitable liquid and solid modifiers include those disclosed and described in U.S. Patents 4,000,105 and 4,154,716. However, any such modifier described therein which fulfills the definition of any of the other components as described in this application are not considered as modifiers but rather as one of the components of the present invention.

Particularly suitable as the modifier or filler substances are fiberglass reinforcement fibers, particularly those having lengths of from 0.16 mm to 1.27 mm and milled glass fibers having a maximum length of 0.16 mm, 0.32 mm and 0.64 mm. Other particularly suitable fillers are mica and wollastonite.

The components which react to form the polyurethane products can be shaped or formed into useful articles by injecting the reactive mixture into molds which are capable of withstanding the exotherm of the polymerizing mass and are nonreactive with and are insoluble when in contact with the liquid reactive mixture. Particularly suitable molds are those made of metal such as aluminum, copper, brass and steel. In some instances, nonmetal molds can be employed such as those made of, for example, polyethylene, polypropylene, polyethylene terephthalate, and silicone elastomers.

The moulded products according to the present invention are prepared by reacting the polyisocyanate and active hydrogen-containing components in a closed mould. The composition according to the present invention may be moulded using conventional processing techniques and are especially suited for RIM applications. In general, two separate

streams are intimately mixed and subsequently injected into a suitable mould, although it is possible to use more than two streams. The first stream contains the polyisocyanate component, while the second stream contains the active hydrogen-containing component and any other additive which is to be included. Particularly suitable injection methods for RIM applications include those disclosed in a paper entitled "The Bayflex 110 Series-The New Generation of RIM Materials," by W. A. Ludwico and R. P. Taylor, presented at the Society of Automotive Engineers Passenger Car Meeting, Detroit, Michigan, USA, September 26-30, 1977; a paper entitled "The Properties of High Modulus RIM Urethanes," by R. M. Gerkin and F. E. Critchfield, presented at the above meeting; British Patent 1,534,258 and a book by F. Melvin Sweeney entitled Introduction to Reaction Injection Molding, Technomics, Inc., 1979.

When injecting a relatively rapid-setting blend into massive metal molds, it may be necessary in order for the molded article to have good surface characteristics, to preheat the molds to an appropriate temperature so that the mold will not abstract the heat of polymerization from the reactive mass and inappropriately delay the solidification time expected of a given formulation. On the other hand, thin wall metal molds could exhibit a minimal "heat sink" effect on relatively large cross section castings and thus, these thin wall metal molds may not require preheating.

The following examples are illustrative of the present invention and are not to be construed as to limiting the scope thereof in any manner.

The following designations, symbols, terms and abbreviations are used in the examples below:

CP 4702	is a glycerine started polyol having hydroxyl number in the range of 33-38 and Average Molecular Weight of 4,700 available from The Dow Chemical Company under the trademark VORANOL CP 4702.
RA 640	is an amine started polyol having hydroxyl number in the range of 615-665 and Average Equivalent Weight of 88 available from The Dow Chemical Company under the trademark VORANOL RA 640.
RM 900	is a modified MDI having functionality of 2.2 and isocyanate equivalent of 180 available from The Dow Chemical Company under the trademark SPECTRIM RM 900.
DETD 80	is diethyl toluene diamine crosslinker available from Ethyl Corporation.
ZnStr	is zinc stearate.
D-400	is an aminated polyoxypropylene glycol having average amine hydrogen equivalent weight of 100 sold by Texaco under the trademark JEFFAMINE D-400.
Dabco 33LV	a 33 percent solution of triethylene diamine in dipropylene glycol, sold by Air Products and Chemicals Inc. under the trademark DABCO 33LV.

- UL-28 is an organometallic catalyst sold by Witco Chemical Company under the trademark Fomrez UL-28.
- A-1100 is amino silane available from Union Carbide Corporation.
- B-8404 is silicone surfactant sold by Th. Goldschmidt under the trademark Tegostab B-8404.
- 5 RM 903 is a modified MDI having functionality of 2.3 and isocyanate equivalent of 170 available from The Dow Chemical Company under the trademark SPECTRIM RM 903.
- MF 7901 is a glass filler available from Bayer AG.
- 10 M342 is a modified MDI having functionality of 2.2 and isocyanate equivalent of 180 available from The Dow Chemical Company under the trademark ISONATE M342.
- MDI is methylenediphenyl diisocyanate.
- Index is the ratio of the amount of reactive isocyanate groups in the reaction mixture divided by the amount of active hydrogen groups in the reaction mixture multiplied by 100.
- 15

The following examples are given to illustrate the invention and should not be interpreted as limiting it in any way. Unless stated otherwise, all parts and percentages are given by weight.

20 Example 1 and Comparative Examples C-1 and C-2

The internal mould release composition was prepared by preblending ZnStr (2 parts by weight) with D-400 (7 parts by weight) at 80°C, cooling the resulting preblend to 60°C and then blending therein jojoba oil (2 parts by weight).

This internal mould release composition was then blended with other components to yield the polyol component shown in Example 1 in Table I.

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Table I

	Example		C-1	C-2	1
	<u>Polyol Component:</u>				
5	CP 4702	parts	93	93	93
	DETDA	parts	28	30	30
	ZnStr	parts	2	2	2
	D-400	parts	7	7	7
10	RA 640	parts	2	0	0
	Oleo Sarcosin	parts	0	1	0
	Jojoba Oil	parts	0	0	2
	B-8404	parts	1	1	1
	UL-28	parts	0.1	0.2	0.1
15	Dabco 33LV	parts	0.1	0.1	0.1

Note: Examples C-1 and C-2 are not examples of this invention.

The RM 903 polyisocyanate component used at Index 110 and the polyol components shown in Table 1 above, maintained at a temperature of 40°C, were introduced into a two-component dosing and mixing apparatus, where a foamable mixture was produced. The reaction mixture was immediately fed under pressure of 180 bars into a steel mould heated to 60°C. The number of mouldings that could be taken out of the mould relatively easy by hand and without the use of levers, a hammer or ejection pins following one application of a soap as the external release agent was measured.

Example 1 produced more than double of releases than comparative Example C-1. Example 1 produces about the same number of releases as comparative Example C-2 but does not destroy the polyurethane catalyst even after 48 hours and does not change the color of the foam to gray.

Example 2 and Comparative Examples C-3 and C-4

The internal mould release composition was prepared by blending ZnStr (2 parts by weight), D-400 (7 parts by weight) and jojoba oil (3 parts by weight) as previously described.

The reaction components shown in Table II below, maintained at a temperature of 40°C, were introduced into a two component dosing and mixing apparatus, where a foamable mixture was produced. The reaction mixture was immediately fed under pressure of 180 bars into a steel mould heated to 55°C. The number of mouldings that could be taken out of the mould relatively easy by hand and without the use of levers, a hammer or ejection pins following one application of a soap as the external release agent was measured.

Table II

	Example		2	C-3	C-4
	<u>Polyol Component:</u>				
5	CP 4702	parts	93	93	93
	RA 640	parts	2	1	1
	DETDA 80	parts	28	28	28
	ZnStr	parts	2	0	2
	D-400	parts	7	0	4
10	Jojoba Oil	parts	3	0	0
	B-8404	parts	1	1	1
	UL-28	parts	0.1	0.1	0.1
	33LV	parts	0.1	0.1	0.1
15	MF 7901	parts	60.31	60.31	60.31

Polyisocyanate Component:

	RM 903 (Index 120)	parts	87.97	87.97	87.97
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20 **Note:** Comparative Examples C-3 and C-4 are not examples of this invention.

Example 2 produced 19 releases with one application of an external mould release agent. Comparative Example C-3 required application of an external release agent after each release of the moulded product. Comparative Example C-4 produced 3 to 4 releases with one application of an external mould release agent.

Example 3

30 The reaction components shown in Table III, maintained at a temperature of 40°C, were introduced into a two component dosing and mixing apparatus, where a foamable mixture was produced. The reaction mixture was immediately fed under pressure of 180 bars into a steel mould heated to 60°C. The demould time was measured and a change in color of the moulded products was observed to determine whether the polyurethane catalyst was destroyed.

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Table III

	Example		3
	<u>Polyol Component:</u>		
5	CP 4702	parts	93
	D-400	parts	4
	ZnStr	parts	2
	DETDA 80	parts	30
10	Jojoba Oil	parts	1
	B-8404	parts	1
	UL-28	parts	0.2
	33LV	parts	0.1
	MF 7901	parts	62.1
15	<u>Polyisocyanate Component:</u>		
	M342 (Index 110)	Index	86

20 The color of moulded products produced in Example 3 was light beige to beige when the active hydrogen-containing component used was blended more than 24 hours before its use. The color of moulded products was dark beige when the active hydrogen-containing component used was blended more than 80 hours before its use which color was attributed to the oxidation of DETDA. This clearly demonstrates that the use of the internal

25 mould release agent of this invention results in substantially no deterioration of the polyurethane catalyst. The dog ear test time was 50 to 55 seconds when the active hydrogen-containing component used was blended more than 24 hours before its use and 60 to 65 seconds when the active hydrogen-containing component used was blended more than 80 hours before its use. This indicates that the reactivity did not change substantially with time.

30 Example 4

 The reaction components shown in Table IV, maintained at a temperature of 40°C, were introduced into a two-component dosing and mixing apparatus, where a foamable mixture was produced. The reaction mixture was then fed under the pressure of 180 to 185 bars into a steel mould heated to 60°C to 65°C. The demould time and number of releases of

35 moulded parts were determined. Also, change in color of the moulded products was observed to determine whether the polyurethane catalyst was destroyed.

Table IV

	Example		5
	<u>Polyol Component:</u>		
5	CP 4702	parts	93
	D-400	parts	7
	ZnStr	parts	2
	Jojoba Oil	parts	3
	DETDA 80	parts	30
10	B-8404	parts	1
	UL-28	parts	0.1
	33LV	parts	0.1
	MF 7901	parts	58.9
15	<u>Polyisocyanate Component:</u>		
	M342 (Index 110)	parts	85.4

20 Within the first 24 hours, the polyol component flow property is good and its reactivity is within normal range. The color of moulded products was light beige. After 24 hours, the reactivity of the polyol component decreased but the color of moulded parts was still beige. The polyol component was left over the weekend (that is, over 84 hours) in the machine under normal impulse circulation conditions at 40°C and 4 bars pressure. The reactivity of the

25 polyol component was the same as within the first 24 hours but the color of moulded products was dark beige. Example 4 produced 20 releases of moulded products with a single application of an external release agent.

Comparative Example C-5

30 The reaction components shown in Table V, maintained at a temperature of 40°C, were introduced into a two-component dosing and mixing apparatus, where a foamable mixture was produced. The reaction mixture was then fed under the pressure of 180 bars into a steel mould heated to 60°C. The number of releases of moulded parts was determined.

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Tabl V

Example

C-5

Poly IC mp nent:

5	CP 4702	parts	74.80
	DETDA	parts	22.5
	Jojoba Oil	parts	1
	B-8404	parts	1.5
	UL-28	parts	0.1
10	33LV	parts	0.1
	A-1100	parts	0.004
	MF 7901	parts	35.20

Polyisocyanate Component:

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RM-900 (Index 110)	60.35
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Note: Comparative Example C-5 is not an example of this invention.

20 Comparative Example C-5 required application of an external release agent after each release of the moulded product. This clearly demonstrates that jojoba oil by itself is not an effective internal mould release agent.

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CLAIMS:

1. An internal mould release composition comprising (a) at least one carboxylic acid metal salt wherein said carboxylic acid contain from 2 to 30 carbon atoms and wherein said metal is selected from Group II of the Periodic Table of the Elements; (b) at least one compatibilizer which compatibilizes said carboxylic acid metal salt in a polyol; and (c) jojoba oil.
2. An internal mould release composition of Claim 1 wherein said carboxylic acid metal salt is present in an amount of from 1 percent to 50 percent, and jojoba oil is present in an amount of from 1 percent to 40 percent.
3. An internal mould release composition of Claim 1 or Claim 2 wherein said carboxylic acid metal salt is selected from the group consisting of zinc stearate, zinc oleate, zinc palmitate and zinc laurate.
4. An internal mould release composition of Claim 3 wherein said carboxylic acid metal salt is zinc stearate.
5. A polyol composition comprising (a) at least one polyol; (b) at least one carboxylic acid metal salt wherein said carboxylic acid contain from 2 to 30 carbon atoms and wherein said metal is selected from Group II of the Periodic Table of the Elements, (c) at least one compatibilizer which compatibilizes said carboxylic acid metal salt in said polyol, and (d) jojoba oil.
6. A polyol composition of Claim 5 wherein said carboxylic acid metal salt is present in an amount of from 1 percent to 50 percent, and jojoba oil is present in an amount of from 1 percent to 40 percent based on the total weight of the carboxylic acid metal salt, the compatibilizer and jojoba oil.
7. A polyol composition of Claim 5 or Claim 6 wherein said carboxylic acid metal salt is selected from the group consisting of zinc stearate, zinc oleate, zinc palmitate and zinc laurate.
8. A polyol composition of Claim 7 characterized in that said carboxylic acid metal salt is zinc stearate.
9. A process for preparing the internal mould release composition of any one of Claims 1 to 4 wherein said carboxylic acid metal salt is preblended with said compatibilizer at an elevated temperature, and then jojoba oil is added to the resulting preblend.
10. A process for preparing polyurethane and/or polyurea products which process comprises mixing and injecting into a suitable mould a polyisocyanate and/or polyisothiocyanate component and a polyol component, allowing the components to react in the mould and then removing the resulting moulded product, wherein said polyol component is the polyol composition of any one of Claims 5 to 8.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/US 96/00372

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B29C33/60 B29C67/24 C08K5/098 C08K5/101 C08K5/17
C08L75/00 C10M159/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B29C C08K C08G C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CHEMICAL ABSTRACTS, vol. 115, no. 22, 2 December 1991 Columbus, Ohio, US; abstract no. 233962y, MASABUMI NAKAMURA ET AL: "Internal mold release compositions" page 80; XP002004119 see abstract & PATENT ABSTRACTS OF JAPAN vol. 15, no. 398 (C-0874), 9 October 1991 & JP,A,03 163127 (SUMITOMO BAYER URETHANE KK), 15 July 1991, see abstract --- -/--	1-8,10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Inter. nal Application No

PCT/US 96/00372

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	US,A,4 471 009 (NORMAN M. PHILLIPS) 11 September 1984 see column 2, line 18 - column 3, line 2 see column 4, line 50 - line 51 ---	1-8,10
A	EP,A,0 173 888 (MOBAY CHEMICAL CORPORATION) 12 March 1986 cited in the application see page 18, line 20 - page 19, line 3; claims 1-12 ---	1-10
A	EP,A,0 250 717 (MOBAY CORPORATION) 7 January 1988 see page 9, line 10-23; claims 1,6,9 ---	1-10
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INTERNATIONAL SEARCH REPORT

Inter national Application No
PCT/US 96/00372

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>JOURNAL OF THE AMERICAN OIL CHEMISTS' SOCIETY, vol. 57, no. 6, June 1980, CHAMPAIGN US, pages 176-178, XP002004118 J.A. CLARKE AND D.M. YERMANOS: "Jojoba - Variability in Oil Content and Composition in a Collection of 1156 Native Plants" see abstract</p> <p style="text-align: center;">-----</p>	1

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Information on patent family members

International Application No

PCT/US 96/00372

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